

AD-764 155

EFFECT OF METAL ADDITIVES ON
COMBUSTION RATE IN PROTOTYPE CARBURETION
SYSTEMS

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1 November 1972

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In Reply Refer to:
FSTC-HT-23-1001-72
DIA Task No. T70-23-01

Date: 1 Nov 72

TRANSLATION

AD 764155

ENGLISH TITLE: Effect of Metal Additives on Combustion Rate
in Prototype Carburetion Systems

FOREIGN TITLE: Vliyaniye Dobavok Metallov na Skorost' Gorenitya
Model'nykh Smesevykh Sistem

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SOURCE: Fizika Gorenitya i Vzryva,
6, 1, Mar 70, pp 93-97

TRANSLATOR: Leo Kanner Assoc.

LANGUAGE: Russian

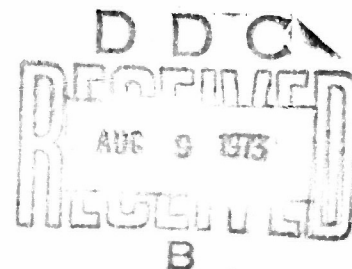
COUNTRY: USSR

ABSTRACT: Additive powders of Al, Mg, B, Zn, Ti, and W in test mixtures of NH_4ClO_4 with bitumen and polymethylene-methacrylate, and of KClO_4 with bitumen, showed that adding finely divided metals to compounds having a weak dependence of combustion rate on pressure strengthens this dependence, whereas if the dependence $u(p)$ is strong for the original compound, additives weaken this dependence. Experimental results agree well with the theoretical model, which allows for simultaneous occurrence of homogeneous reaction between products of gasification of oxidant and or organic fuel, and the heterogeneous reaction of combustion of metal particles.

COUNTRY CODE: UR
SUBJECT CODE: 21

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KEY WORDS: Metal additive
Combustion R&D
Combustion rate
Test method
Combustion theory
Fuel oxidation



FICHE: FD70/605017/E12

Reference [1] considered the effect of metal particle additives on the rate of combustion of mixtures of lightly carbureted fuels and oxidants. It was shown that the effect of metal additives is determined first of all by the particle size d_M . Sufficiently large metal particles will only reduce¹ the rate of combustion, since their effect depends slightly on the nature of the metal and of the oxidant, upon the fuel-oxidant ratio, upon the particle size of the oxidant, and on pressure. On the other hand, metal granules which are thinly enough dispersed can significantly increase the rate of combustion. The present article considers the effect of finely divided particles of metal in greater detail.

Experiments were carried out with test mixtures of ammonium perchlorate (PCA) with bitumen and polymethylene-methacrylate (PMMA), and also mixtures of potassium perchlorate (PCK) with bitumen. Aluminum powders² with an effective particle size of ~ 2.7 - 3.0 and ~ 12 μ were used, as well as aluminum granules with an effective particle size of ~ 0.09 , ~ 0.2 , ~ 5 , ~ 8 and ~ 15 μ^3 . In addition, a few series of experiments were run with powders of magnesium $d_M = 10$ μ , of boron $d_M = 1$ μ^4 , of zinc $d_M = 6$ μ^4 , of titanium $d_M = 16$ μ^4 and of tungsten $d_M = 2.5$ μ^4 . In the aluminum powders the shape of the particles was flaky; in granules they more or less approximated the spherical. The range of particle sizes in almost all cases was very wide (especially for aluminum flakes); the sole exceptions were granules of Al and Mg obtained in the laboratory of M. Ya. Gen. The method for preparing the mixture was the same as in references [2, 3]. The metal granules were introduced at a constant ratio of oxidant and organic fuel. The experiments were performed with charges 6 - 8 mm in diameter and 8 - 10 mm high in a gas "bomb" of constant pressure in nitrogen. The rate of combustion was measured with a piezo-electric pressure transducer.

¹With an admixture of $\sim 15\%$ Al or W in granule form, the rate of combustion is usually cut by 5 - 15%.

²The size is calculated by size of unit surface, as measured by a PSK-2 device.

³Granules with a particle size of ~ 0.09 and 0.2 μ were obtained in M. Ya. Gen's laboratory (IKHF AN SSSR); their size was determined by electron microscope; for remaining granules the unit surface was measured with a PSK-2.

⁴Size was calculated by size of unit surface.

TABLE 1

d_m, μ	z				
	1 atm	6 atm	11 atm	51 atm	101 atm
~ 12	1.08	1.14	1.03	1.10	1.14
~ 3	1.23	1.26	1.33	1.21	1.38
~ 0.09	1.94	1.58	1.55	1.69	1.63

The effect of the metal additive was traced by using parameter $z=u/u_0$, where u, u_0 are, respectively, the combustion rate of the mixture with and without the metal additive.

EFFECT OF PARTICLE SIZE OF A METAL

According to the degree of reduction of the particle size of a metal, its effect on the combustion rate is increased which can be observed from a sample of the mixture PCA ($\sim 10\mu$) bitumen at $a = 0.75$ with 13.1% aluminum additive (concerning three mixtures) (table 1).

TABLE 2

d_m, μ	z				
	6 atm	11 atm	41 atm	61 atm	101 atm
15	1.04	1.06	1.03	1.01	1.13
8	1.04	1.01	1.16	1.18	1.41
2.7	1.15	1.18	1.21	1.27	1.53

EFFECT OF THE AMOUNT OF ADDITIVE

The effect of the amount of additive was examined for stoichiometric mixtures of PCA-bitumen and PCK-bitumen with an aluminum additive (~ 0.09 and 0.2μ). For increases in the amount of additive in limits to $\sim 30\%$, its activity is strengthened as shown in table 3, Mixtures of PCA + Bitumen with Aluminum Additive Al ($\sim 0.09\mu$).

TABLE 3

Particle size PCA, μ	% of aluminum additive	z				
		1 atm	6 atm	11 atm	51 atm	101 atm
10	6.5	1.15	1.07	1.07	1.04	—
	13.1	1.72	1.63	1.55	1.65	—
	31.1	3.46	3.46	3.80	—	2.87
180	13.1	1.85	1.73	1.76	1.62	1.51
	31.1	3.41	3.02	2.78	2.70	2.37

For a mixture of PCK ($\sim 10\mu$) + bitumen with additives of 6.5; 13.1; and 31.1% Al ($\sim 0.2\mu$) at 11 atm, values of $z = 2.02$; 2.31 ; and 2.74 were obtained respectively, and at 101 atm, values of $z = 1.34$; 1.69 ; and 2.4 were obtained respectively.

The absolute value of the combustion rate of compositions with finely dispersed oxidants and with a large percent of finely dispersed aluminum is extremely high as shown in table 4 for mixtures containing 31% Al ($\sim 0.09\mu$).

TABLE 4

Mixture	μ , mm/sec				
	1 atm	6 atm	11 atm	51 atm	101 atm
PCA + bitumen; $a = 1$	5.40	19.5	32.3	56.0	86.1
PCA + bitumen; $a = 0.75$	5.75	15.5	25.8	60.8	—
PCK + bitumen; $a = 1$	—	—	18.4	43.4	79.0

It follows to note that the dependence of z to a and the particle size of an oxidant (d_{ox}) for bitumen based mixtures is relatively weak. At high pressures, z decreases as d_{ox} increases.

EFFECT OF THE NATURE OF A METAL

Results of experiments according to the effect of the nature of a metal on the value z are approximations since each metal (except Al) was tested according to only one fraction, with the average size of particles varying from one metal to the next. Experiments with a stoichiometric mixture of oxidant ($\sim 10\mu$) with

bitumen, where 13.1% of metal was introduced, have shown that the combustion rate can be significantly increased by means of additives of finely divided Al, B, and Mg (table 5).

However, the particle sizes of magnesium, and to some slight degree boron, were too large, so that the potentialities of these metals in a mixture for increasing combustion rate are insufficiently explained.

Titanium additives only negligibly (by 5 - 15%) increased combustion rate; however, the particle size ($\sim 16\mu$) was too large.

TABLE 5

Oxidant	Metal	d., μ	z				
			1 atm	6 atm	11 atm	51 atm	101 atm
PCA	Al	~ 0.09	1.72	1.63	1.55	1.65	—
		~ 12	1.31	—	1.29	1.14	1.14
	B*	~ 1	1.32	1.24	1.20	1.27	1.19
	Mg	~ 10	1.97	1.72	1.58	1.30	1.20
PCK	Al	~ 0.2	6.45	2.72	2.31	1.65	1.69
		~ 12	1.44	1.30	1.20	1.06	1.04
	B	~ 1	4.22	1.95	1.84	1.20	0.95
	Mg	~ 10	3.10	1.84	1.72	1.13	0.90

* Boron is a non-metal, but for the sake of brevity this is not specified.

Additives of W and Zn were ineffective in increasing combustion rate: $z \approx 1 \div 1.1$ was obtained for W ($\sim 2.5\mu$) and $z \approx 0.9 \div 1.1$ was obtained for Zn ($\sim 6\mu$).

Effect of Metal Additive on Dependence $u(p)$

The experiments performed showed that for some mixtures the metal additive had a strong effect at lower pressures and a weak effect at high pressures, and for other mixtures the opposite was true. The following general trend could be established.

1. If the dependence $u(p)$ is weak for the original (without metal) mixture (the exponent in the combustion law $v_0 < 0.5$), then the metal additive strengthens the dependence $u(p)$ (i.e., the additive increases the combustion rate slightly at low p and strongly at high p). Correspondingly, the exponent v is higher than v_0 for the mixture with metal.

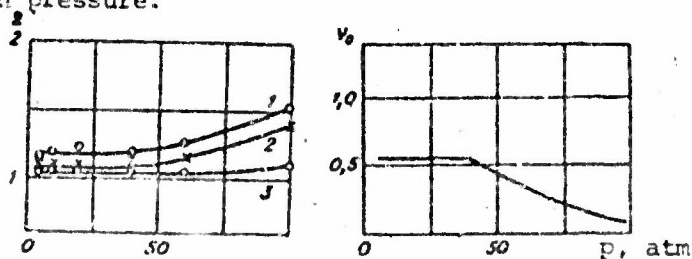
2. On the other hand, if the dependence $u(p)$ is strong for the original mixture ($v_0 \geq 0.5 - 0.6$), the metal additive weakens the dependence $u(p)$, and correspondingly $v < v_0$.

Thus, for example, $v_0 = 0.57$ for a stoichiometric mixture of PCA ($\sim 10 \mu$) plus bitumen. When Al, Mg or B are added, the value of v falls within limits of $0.44 - 0.56$, i.e. is negligibly decreased. For a mixture of PCA ($\sim 180 \mu$) and bitumen at $\alpha = 0.75$ and $\alpha = 1$ $v_0 \approx 0.54$. When Al of various sorts is added, the value of v lies within limits $0.42 - 0.50$.

On the other hand, for a stoichiometric mixture of PCK ($\sim 10 \mu$) plus bitumen with a high value of $v_0 = 0.75$, adding finely dispersed Al, B and Mg markedly weakens the dependence $u(p)$:

Additive	d_M, μ	v
Al	~ 0.2	0.61
Mg	~ 10.0	0.45
B	~ 1.0	0.43

As follows from the figure, exponent v_0 for a gelatinated mixture of PCA ($\sim 6 \mu$) plus PMMA depends on the pressure range. At $p \leq 40$ atm, when $v_0 \approx 0.55$, the magnitude of z scarcely depends on p at all. However, as soon (at $p \geq 50$ atm) as the exponent v_0 becomes less than 0.5, the magnitude of z begins to increase with pressure.



Relationship between dependence $z(p)$ for mixture PCA ($\sim 6 \mu$) + PMMA + 10% Al at $\alpha = 0.88$ and dependence $v_0(p)$ for original mixture (without Al additive). 1 - $d_M \approx 2.7 \mu$, 2 - $d_M \approx 8 \mu$, 3 - $d_M \approx 15 \mu$.

Discussion of Results

The effect of metal additives on combustion rate can be explained on the basis of the thermal theory of combustion and concepts about the zone of effect [4].

Particles of a metal can increase the rate of combustion of a mixture only when they ignite and effectively burn up near the surface of the charge. Additives of such metals as Mg, B and especially Al increase the temperature of combustion. As to the rate of combustion, then its increase is linked not only with the emergence of additional heat release due to combustion of metal particles, but also with increase of rate of heat release due to reaction of products of gasification of the basic mixture as a result of increase of combustion temperature.

In reference [5] an expression was obtained for the rate of combustion during simultaneous occurrence in one narrow zone of homogenized reaction in the volume and also heterogeneous reaction on the particles. With regard to the case of interest to us, combustion of particles of metals, which occurs in a diffusion regime, the expression for the magnitude of z assumes the form

$$z \sim \sqrt{\exp \left[\frac{E}{R} \left(\frac{1}{T_r} - \frac{1}{T_r'} \right) \right] \cdot p^{1-2\nu_0} \frac{A'}{d_w^2} \exp \left(\frac{E}{R T_r} \right)}. \quad (1)$$

where E is the energy of activation; T_r' and T_r are, respectively, the combustion temperatures of the mixture with and without metal.

If T_r' does not depend on temperature, then from (1) we obtain

$$z \sim \sqrt{A + B p^{1-2\nu_0}}. \quad (2)$$

From (2) it follows that at $\nu_0 < 0.5$ z should increase with increase of p , and at $\nu_0 > 0.5$ it should decrease. This result is found to agree well with experimental data¹.

We also note that according to (1) z should increase with decrease of metal particle size and of combustion temperature of the original mixture T_r . More recently it has been indicated that, other conditions being equal, it is easier to increase the rate of combustion of a "cold" mixture (if, of course, the metal particles are able to ignite and burn). Both these results agree with experiment.

In discussing the results of the experiments we must keep in mind the following complicating circumstance. Undoubtedly in the process of preparing the charge, nodulizing of the metal particles occurs to this or that degree. Moreover, on the surface of the burning charge one may observe amalgamation of a certain portion of the melted particles, resulting in the formation of

¹Strictly speaking, (1) and (2) are applicable only to mixtures with a finely dispersed oxidant, however, as was noted above, increase of d_{ox} does not influence experimental values of z too strongly.

comparatively coarse cupels [6, 7]. In other words, the actual sizes of particles igniting and burning under the surface of the charge can exceed the size of the particles of the original granules (d_M), and this does not exclude the possibility that a sharp decrease of d_M may slightly decrease this actual size of particles.

Thus, we have studied the effect of finely divided metal additives (Al and to a significantly lesser degree Mg, B, Ti, W, Zn) on the combustion rate of test mixtures of PCA and PCK with bitumen and PMMK.

It has been found that the smaller the size of the metal particles and the greater their quantity (at least up to 30%), the less the additives of finely divided metal will increase the combustion rate.

Adding finely divided metals to compounds having a weak dependence of combustion rate on pressure strengthens this dependence. On the other hand, if the dependence $u(p)$ is strong for the original compound ($v_0 > 0.5$), additives weaken it.

Results of the experiments succeed well enough in totally explaining concepts about the zone of effect, as well, based on thermal theory of combustion. The effect of metal on the dependence $u(p)$, and also the strengthening of the efficacy of metal in the presence of inert diluent, agrees well with the theoretical model, which considers simultaneous occurrence of the homogeneous reaction between products of gasification of oxidant and of organic fuel, and the heterogeneous reaction of combustion of metal particles.

Submitted July 22, 1967

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